KINETICS OF THE OLEFINE-BROMINE REACTION

Part VI. Further Consideration of the Arrhenius Parameters

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IT is well known that in the treatment of any kinetic problem the activation energy is a factor of fundamental importance. In any reacting system, the reactants and products represent states of minimum potential energy, while the transition state must be a maximum in between these limits of minima. The reaction involves the breaking of bonds and the formation of new ones and the work done in the process constitutes the activation energy. When the reaction of a series of similar compounds are studied, the principal difference that may be expected is in the activation energy. One cannot, however, consider the variation in the other Arrhenius parameter negligible as has been demonstrated by the work of Hinshelwood and co-workers.[5, 7, 8]

Though the number of compounds investigated in the present series is as yet small, one has still to consider these parameters as the influence of substituent groups on these is of considerable diagnostic value and is of greater significance than any measurement of velocity constants at a single temperature. Since the reaction in question involves the change of a double bond to a single one, rupture of the bond between the atoms of the bromine molecule and the formation of carbon-bromine bonds, one may expect a more or less constant frequency factor† while the activation energy shows systematic variations. The results of evaluating these and the Log $k/1/T$ curve used for the purpose are given below in Table I and Fig. 1.

An examination of both the figure and the table clearly shows that substituents alter both the energy of activation and the frequency factor. The activation energy in its turn can be further analysed into the bond energy

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† The quantity of the Arrhenius equation which is approximately kT/h and hence has the dimensions of frequnecy. This term is preferred to the older ' probability factor '.
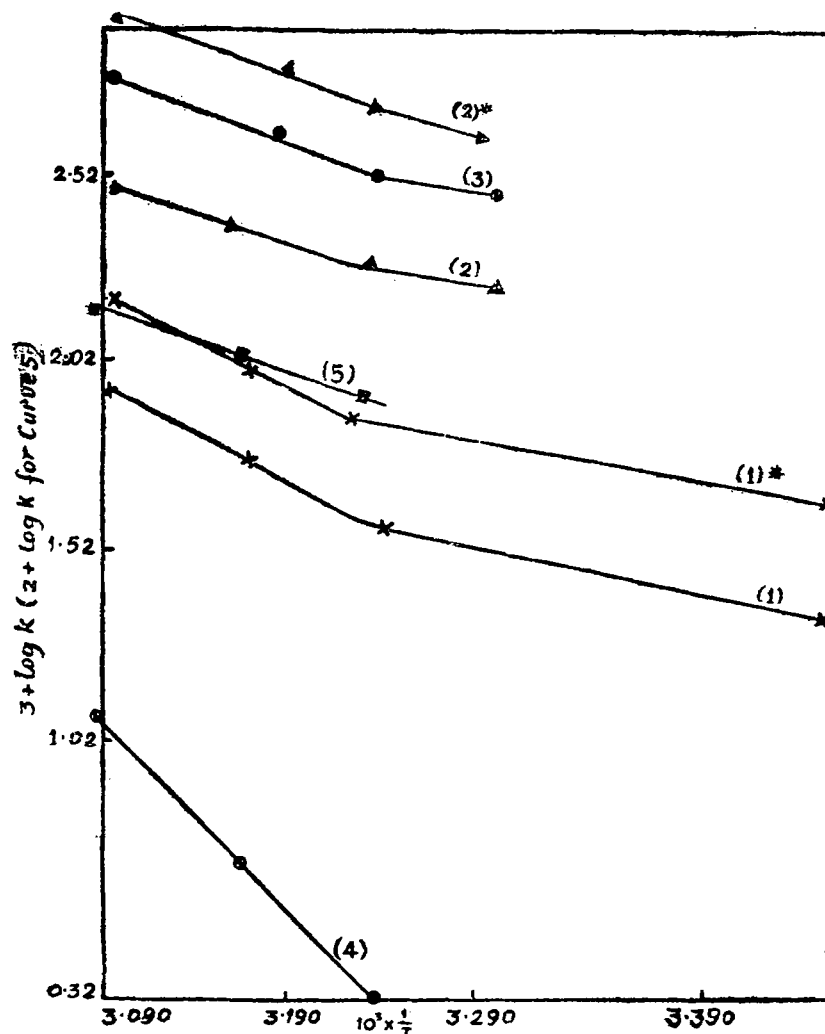
Fɪɢ. 1. log $k/1/T$ curve

and forms ψ_2 and ψ_3 will have identical energies only in the case of symmetrically substituted olefines. Additive reactivity depends primarily on the opening up of the double bond and will naturally depend on the relative contribution of the different structures which in its turn determines the bond energy as well as the repulsion energy. With unsymmetrically substituted olefines the contribution by the ionic structures can be quite appreciable and when this is combined with the presence of groups that facilitate reaction with electrophilic reagents on account of their influence on the state of polarisation of the molecule, the activation energy can be substantially

lower than that for the unsubstituted ethylene. No experimental data is available at present for the activation energy, for the reaction between ethylene and bromine but Sherman[13] using Eyring's method[3] has evaluated by using the transition state method that this has a value of about 23 Kcal. The expectation is substantiated by our values for the monobasic acids studied. A similar reduction in activation energy can be expected with substituents of Class 7 ($\pm$ T)[9] which can stabilise the carbonium ion of the first stage of bromine addition even if symmetrical disubstituted compounds are considered. The results with stilbene clearly bears this out.

On the other hand with deactivating groups, an increase in the activation energy is offset by the resonance energy, so that even with symmetrical disubstitution products like fumaric acid, the observed energy of activation is not far from the calculated value for ethylene itself.

A close examination of the log $k - 1/T$ curve of the first three compounds in the table reveals a definite change of slope below 25° C., indicating that the reaction is a composite one.[6] The very low value for the activation energy in the lower temperature region suggests a termolecular reaction changing over to a bimolecular one at the higher temperatures. This feature appears to be independent of concentration changes as may be noticed from the fact that this results only in a parallel shift of the log $k - 1/T$ curve. (Starred figures in the figure refer to higher concentrations.) The observations of Robertson and co-workers[12] with a number of olefines at 25° C. then becomes quite understandable. Considerable variations in rate constants can be accounted for solely by changes in activation energy but our present data are inadequate for a complete analysis. Mention should, however, be made here of the pronounced catalytic effect of hydrogen halides (or more accurately by hydrogen ions). The calculations of Polanyi[1, 11] have shown that the proton affinity of ethylene is of the same order of magnitude as that of water and as such association of a proton prior to the addition reaction can be expected to facilitate the change by providing a seat of attack. A corollary to this one has to expect that attack by nucleophilic bromine will not be facilitated by the same catalyst.

Turning now to the other parameter, namely, the frequency factor, a normal second order reaction requires a value of the order of 10^9 while the values in the table show considerable variations from this. A point of particular interest is the fact that fumaric acid appears to react much faster than it should (a bimolecular reaction with an activation energy of 20 Kcal. should give a rate constant of the order of 10^{-12} with a frequency factor of normal value but observed values are much higher. The remaining four

compounds react with bromine at rates that bring them under the category of " slow " reactions. This is only to be expected when one considers the nature of the reaction. For the reaction to take place, encounters have to be made between molecules possessing the requisite activation energy. Secondly, the initiation of attack is by an electrophilic reagent. Further, the encounter between the reactants must be in the right phase in the region of the double bond. As a first approximation, one can consider that the ratio of the number of effective collisions, z^*, to the total number of collisions calculated in the usual manner, z, will be proportional to the area of the strip cut on the spheroid of the dimensions of the molecule by two parallel planes perpendicular to the direction of the reacting bond, a_s, to the total area of the surface of the spheroid, a. Taking the surfaces as functions of the square of bond distance r_b and major axis of the ellipse r_m, we have

$$z^*/z \simeq (r_b/r_m)^2.$$

Taking into account the fact that the rate determining step in the reaction involves only one of the two doubly bound carbon atoms, this ratio should be halved in the present case. All the compounds studied here have major axes of the order of $6 - 11$ Å while the carbon-carbon double bond distance is only $1 \cdot 33$ Å. As a consequence, the frequency factor may be expected to be reduced from 10^9 to about 10^6, a value not far from the ones obtained.†

A further complication that one has to consider in the study of unsaturated compounds of the polysubstituted olefine group is the isomerisation of *trans* compounds to the *cis* form. This complication is absent only in the case of $\beta\beta$-dimethylacrylic acid in the present series. Unpublished observations of the authors indicate that *cis* crotonic acid is less reactive than the *trans* while maleic acid is considerably more reactive than fumaric acid. It is well known that halogens facilitate the interconversion of these stereoisomeric forms[2, 10] and this can easily account for the observed anomalies in the frequency factor. Another contributory cause for reduction in the frequency factor is the composite nature of the reaction.

In a number of reactions, a close correlation is observed between log PZ and $1/E^{\frac{1}{2}}$[5] and a similar relationship may be looked for in the present reaction also. For the sake of comparison the product of these two quantities has been taken for Table II.

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† A more rigorous analysis of this and other " slow " reactions will be communicated shortly.

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TABLE II

Substance		Log PZ × 1/E
Crotonic acid	..	0·056
Tiglic acid	..	0·046
Dimethylacrylic acid	..	0·047
Fumaric acid	..	0·011
Stilbene	..	0·050

It will be observed that the product is constant within the limits of experimental error, the exception being provided by fumaric acid. The significance of this can be considered only after a fuller investigation.

SUMMARY

An analysis of the Arrhenius parameters for the addition reaction indicates that the reaction is a composite one and of the " slow " type. The influence of substituents on the energy of activation and on the frequency factor is discussed and the abnormal values of the latter are accounted for. A close correlation is also noticed between the two.

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